AD-A008 849

RESEARCH AND DEVELOPMENT IN THE GLASS FIBER SODIUM-SULFUR BATTERY

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Prepared for:

Advanced Research Projects Agency

31 December 1974

Semi-Annual Technical Report

December 31, 1974

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Contract No. DAHC-15-73-C-0254

Sponsored by

Advanced Research Projects Agency
ARPA Order No. 2381

Submitted by

The Dow Chemical Company
Walnut Creek, California

Program Code 5D10
Effective: March 27, 1973
Expiration Date: June 30, 1975
Contract Amount $528,241

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SUMMARY

I. Technical Problems

The electrochemical characteristics of the hollow fiber sodium-sulfur cell have been shown to be outstanding. The major problem now is to obtain increased lifetimes with the same good performance. We want to demonstrate long life (years) with many thousands of charge-discharge cycles in cells that do not change internal resistance with total time in operation.

The heating-cooling characteristics of the cells still needs to be determined.

II. General Methodology

Cell failures are almost always associated in some way with failure of the glass fibers. We are pursuing two approaches toward increasing the cell life. One is a "brute force" approach of increasing the wall thickness of the fibers. The other approach is to find out what is causing the glass membrane to break.

In the first approach, cells are being constructed using thicker walled glass fibers. Plots of cell lifetime versus fiber wall thickness give an indication of the effectiveness simply using thicker fibers to get longer lives. Where there is an indication of some presumed harmful contaminant in the system, such as water, the contaminant is removed as much as possible. The indication of effectiveness, again, is increased lifetime of the cell.

The second, more fundamental approach of discovering the causes of glass fiber breakage is more involved. Cells containing any where from 6 to 3000 fibers are made under varying conditions operated at different rates and depths of discharge, and in the presence or absence of various impurities. The glass fibers and the tube sheets are tested for changes in appearance or strength after being subjected to exposure or strain. Information concerning factors that cause early cell failure in these small cells is utilized in building better large cells which will have better durability.

III. Technical Results

During this period, new records of lifetime were set on both the 5 ampere-hour and the smaller 0.3 - 0.4 sampere hour cells. One 5 ampere-hour cell operated 23 days before failure. However, during this time the internal resistance of the cell increased many-fold. Another 5 ampere-hour cell operated for over 14 days, charging and discharging on 4 hour cycles with no change in internal resistance. We confirmed that it is necessary to treat the glass fibers with BCl_3 gas before filling them with sodium if the cell resistance is to be kept constant for more than 5 - 7 days.

The smaller 0.3 - 0.4 ampere-hour cells containing 1000 fibers have run continuously as long as 68 days (over 1000 hours) on charge-discharge cycling. Cell resistance increased only a few percent. Cycling was done on one hour cycles at the 3 hour rate.

While charge-discharge rates at three times the design rate shorten cell life, decreasing the rates from design rate to 1/3 of design rate does not increase lifetime.

Thicker walled fibers do indeed give longer lifetimes to the cells. Thousand fiber cells last 20 - 27 days when made of 10 micron wall fibers. We are now running cells with 20 micron wall fibers after experiencing some difficulty in drawing good fibers with this size wall.

Fiber failure is probably not caused by corrosion due to an impurity such as Na_2O from the sodium side of the membrane. This was shown by concentrating the sodium impurities in the fiber during cell operation and seeing no decrease in cell life.

We returned to using fiber glass containing excess NaCl in order to take advantage of the increase in conductivity. Cells made from fiber glass containing no chloride ion did not show any lifetime increase over the cells made from the chloride containing glass, so chloride ion in the glass is presumably not harmful.

The spinning and assembly of the glass fibers is continually improving. No problems appear in spinning after many successive runs using the platinum-lined furnace. Wider fiber to fiber spacing and improved designs of the hot N_2 fiber cutter have decreased the number of double fiber seals. When positioning shoes were used for fiber lay-down, cell life was shortened, probably by scratching the fiber.

Nitrogen could be used as the cooling gas at the spinning orifice instead of helium but flow rate adjustments become critical. Various designs of cooling jets were tried.

Some experiments on using a CO_2 laser for cutting and sealing the glass fibers were begun. The first results were encouraging although the focus adjustment seems critical.

Attempts were made to improve the tube sheet tightness and decrease the fiber weakening at the tube sheet fiber interface by varying the solder glass particle size distribution and by putting additives into the solder glass to adjust the expansion coefficient. No improvement was seen.

Some 5 ampere-hour cells have been made and run using 125 micron spacing between adjacent foils rather than 100 micron spacing. This is a possible change in design which might be beneficial if a 6-8 hour cell is desired rather than a one hour cell. Smaller cells using 125 micron to 178 micron foil to foil spacings were also built and run.

Weakening of the glass fibers at the tube sheet interface was greatly improved when the tube sheet material was changed from 94% B_2O_3 - 6% Na_2O to 95-1/2% B_2O_3 - 4-1/2% Na_2O and the tube sheet fused at 374°C instead of 385°C. With this material, not only is the fusion temperature lower, but the expansion coefficient is closer to that of the fibers. Cells made using this tube sheet material have longer lifetimes.

Another cause of shortened cell life has been badly distorted seals at the fiber ends. This has been identified, and, for the most part, corrected.

Experiments on possible attack by Na_2S_4 on the fiber tube sheet junction have been started. Preliminary results indicate no detectable attack.

IV. Implications for Further Research

Although some of the causes of cell failure have been found and corrected, others remain. A tube sheet glass of 96% B_2O_3 - 4% Na_2O, having a lower fusion temperature will be tried. Thorough drying of the tube sheet glass will remove another possible cause of failure. Thorough drying of the fiber and foil assembly before filling the cell will remove more of the sources of original cell contamination.

The lifetimes of the five ampere-hour cells are now long enough so cell operating characteristics at various rates and depths of charge-discharge can be determined. The wider foil to foil spacing and fiber to fiber spacings which would be used for cells designed for the 6 - 8 hour rate change the cell resistance characteristics on the charge cycle.

Lifetime data on cells with 15 micron, 20 micron, and 25 micron glass walls will continue to be gathered.

INTRODUCTION

This is a semi-annual technical report on Research and Development of the Glass Fiber Sodium-Sulfur Battery. It covers the period July 1, 1974 to December 31, 1974.

The work is being done under a contract sponsored by the Advanced Research Projects Agency and jointly funded by the Advanced Research Projects Agency and The Dow Chemical Company.

Under the terms of the Contract, we are to try to make multi-fiber cells capable of at least 1000 cycles of charge-discharge, build larger cells capable of long lifetimes, scale up to the 5 ampere-hour cell, continue development of a 40 ampere-hour cell, determine operating parameters at different charge-discharge rates, and determine construction details necessary for thermal cycling.

Good progress has been made. At the beginning of this reporting period, cells containing 1000 fibers had operated up to one month, and the 5 ampere-hour cell had operated for 14 days, although its internal resistance increased during its lifetime. Now, the 1000 fiber cells are still operating at 68 days (over 1600 hours) of continuous charge-discharge, and the 5 ampere-hour cells have operated 14 days with no increase in internal resistance.

RESULTS

I. Back-up for Fabrication Operations

Glass Making. At the time of the last report, we were using two different glasses for the fiber glass. They differed in that glass #406 contained 4.8 mole % NaCl in order to increase the conductivity . The other, glass #410 had no NaCl, and its conductivity was about 1/15th that of the #410. Preliminary results had indicated that the Cl free glass gave longer-lived cells. These results were not confirmed and the chloride containing glass is now used to take advantage of the higher conductivity.

The #406 is a borate glass container 60.5 mole % B_2O_3. This is on the border line of glass stability in the $Na_2O \cdot B_2O_3$ system. We made some glass similar to the #406, but with added B_2O_3 (65 mole%) to stabilize the glass (#413). Cell lifetime of cells made with this glass did not seem to increase, and, since the conductivity of the glass was less than the conductivity of the #406 by almost a factor of two, we discontinued using the #413 glass.

The composition of choice for the fiber glass is still the #406 glass. Its expansion coefficient is 121×10^{-7} per °C.

The tube sheet glass being used at the time of the last report was 94% B_2O_3 - 6% Na_2O. Its expansion coefficient is 111×10^{-7} per °C. A possible reason for the weakening of the fibers at the tube sheet fiber interface was thought to be the difference in expansion coefficient. Small amounts of another non-fusable high expansion glass were added to the tube sheet glass mix. This was to increase the bulk expansion coefficient to match that of the fiber, and yet, since the additive would not melt, it would not affect the fluxing properties of the tube sheet glass. Using this combination, the fibers were still weakened when the tube sheet was fused.

Tube sheet glass was then made from 95-1/2% B_2O_3 - 4-1/2% Na_2O. The expansion coefficient is 116 x 10^{-7}, much closer to the 121 x 10^{-7} value of the fiber glass. The transformation temperature is about 323°C and the "melt temperature", under a 2.5 gram load is 363°C. This tube sheet glass could be fused at 368°C - 374°C. At this fusion temperature, the fibers are much stronger at the tube sheet. We do not know whether they are stronger due to the lower fusion temperature or due to the closer match in expansion coefficients. We are now making a 96% B_2O_3 - 4% Na_2O to try as tube sheet glass. There is some concern that the melting point of this glass is quite low.

Solder Glass Making. The tube sheet is made by extruding a paste of sieved fractions of the ball-milled solder glass. It is important that the paste have as high a solids content as possible so that there is minimum shrinkage in subsequent fusion. A "standard" paste is made by mixing 7.0 grams of the solder glass powder with 0.7 grams of cumene. We have noticed that when the solder glass powder is very dry, a good useable paste can be made using as little as 0.58 grams of cumene to 7.0 grams of powder. In order to try to keep the powders dry, the pastes are now mixed in a special low humidity room, where the relative humidity is kept at less than 2%. There is still some water pick-up but it has greatly lessened.

Purification of the Reactants. The sulfur is purified as described in previous reports by distilling it at 800°C and then purging with N_2 to get rid of CS_2 and H_2S.

During this report period, we have begun to "purify" the sodium by filtering at 110-120°C through a medium fritfilter. This removes the large bulk particles of Na_2O.

II. Modification of Miniplants

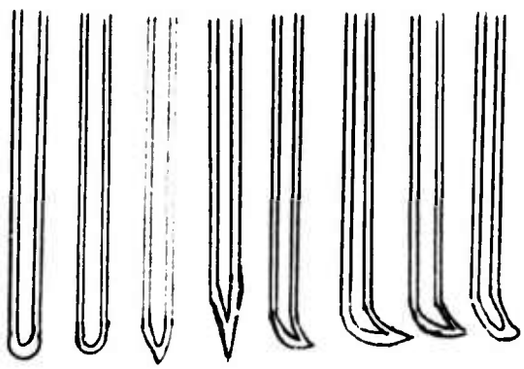
Fiber Drawing and Assembly. The platinum-lined melting furnace and platinum spinnerette continue to work well. Many, many spinning runs have been run with the furnace. A hole developed in the platinum lining where excess flux was used in making and welding the lining. A new lining was obtained and readily installed. The outside of the nickel bodied furnace became badly corroded from oxidation and was repaired by a nickel spray-on technique. A small particle of solid - - - possibly carbon - - - fell into the glass melting tank and became lodged in one of the glass-feed holes in the spinnerette. The furnace was washed out and the particle removed with no apparent harm to the furnace.

Cooling the drawn fiber at the spinnerette is still a problem. When cooling is done correctly, the fiber is uniform with a centered hole, and is drawn in a stable manner. Various types of cooling nozzles have been designed and built to try to make placement of the nozzles less critical. If the fiber is drawn at a high rate of speed, or nitrogen is used as a cooling gas instead of helium, the placement of the cooling nozzles and the cooling gas flow rates became even more critical. The cooler presently being used is an array of ten nozzles. The two upper nozzles blow helium as a cooling gas and the lower nozzles blow nitrogen.

The fiber take-up machine has been improved during the last few months. The problem of laying down the fibers in a parallel manner with precise spacing has not been solved, but the results are improving. The use of placement "shoes" to position the fiber gave resulting cells with shorter lifetimes. The shoes apparently scratched the fiber. Without the laydown shoes, no scratches can be seen on the fiber surface using scanning electron microscope techniques at 1000X. For cells that are designed to be longer than one hour cells, the close and precise spacing is not necessary and the problem is easier. For the one hour cell the

fibers are spaced about 100 microns apart. For the longer rate cells, the fiber-fiber spacing can be up to 200 microns. At this spacing, we get only a few "double seals" at the fiber ends. An important cause of these "double seals" seems to be a movement of the fiber after it has been laid down but before it passes the hot nitrogen cutter-sealer. This is being corrected.

The use of the hot nitrogen stream to cut and seal the fibers has given erratic results. Sometimes instead of sealing the individual fibers in a smooth spherical manner, the seal is in the form of a point or a hook:



This puts weak spots in the fiber that are susceptible to later breaking. A part of this problem, also, seems due to the fact that some fibers are not in the proper "focus" as they go through the hot gas cutter. Helium was tried as a cutting gas rather than nitrogen, but the temperature and flow rate settings were even more critical. Some experiments were done using a CO_2 laser to do the cutting and sealing of the fibers instead of hot gas. The first results indicate that the focus is also critical using the laser.

III. Cell Assembly

The cell assembly machine has not been changed much during this period. A number of cells were made with 125 micron and 175 micron spacings

between successive foil rolls instead of the "standard" 100 micron spacing. As mentioned before, cells designed for the three or six hour rate would preferably have wider foil to foil spacing as well as wider fiber to fiber spacing. These cells assembled with no trouble and operated in a satisfactory manner.

The use of 95-1/2% B_2O_3 - 4-1/2% Na_2O as tube sheet glass has not changed the assembly techniques except for the lower temperature of fusion for the tube sheet. Since the glassed edge of the anode cup is the same composition as the tube sheet glass composition, sealing the anode cup onto the tube sheet can be done at a slightly lower temperature then when using the 94% B_2O_3 - 6% Na_2O solder glass.

The cells are now loaded with sodium and sulfur, raised to operating temperature and sealed - - - all in the N_2 filled dry box, and then brought into the laboratory environment for operation. Air leaks into the cells greatly shorten their lifetimes, so sealing is important. Since our present cells have glass envelopes, seals are made by Apiezon Wax in areas that do not get above 100°C.

IV. Testing and Evaluation of Cells

Two different types of cells are used in the testing and evaluation program. The smaller size is a 1.1 cm diameter fiber bundle containing 1000 fibers with 5 cm of working length. These are the T-numbered cells in Table I. They are nominally 0.3 - 0.4 ampere-hour cells. The larger size cell is a 5 ampere-hour cell consisting of 3000 to 7000 fibers. It has a 1.65 cm diameter fiber roll and the fiber working length is about 8 cm long. This cell is designed so that the construction details can be directly scaled up to larger sizes. These are the A-numbered cells in Table II.

The T-cells are used in most of the work to test the effects of changing parameters or conditions. The results are then re-tested in the larger cells.

TABLE I

1000 FIBER CELLS

Cell	Fibers Glass	Fibers Size, μ	Fibers Wall, μ	Current Density ma	Cycles, Hrs.	Depth, %	Na°, Column Volms	Life Days	Remarks
T-73	406	70 x 50	10	940	.16	25	0.9	9	Probable Fiber Failure
T-76	"	"	"	230	1	42	1.4	25	Out of Na, corroded lead
T-78	"	"	"	210	1	35	1.3	27	
T-82	410	"	"	70	1		.43	18	Hole in fibers under tube sheet - Bad Seal.
T-83	406	"	"	1000	.6	>90		7 (160 cycles)	Zr/Ti, air leak
T-84	410	"	"	70	1		.43	19	Broken fibers below tube sheet.
T-85	406	"	"	125	1		.76	21	Zr/Ti, Fiber failure under tube sheet.
T-87	"	"	"	900	.6	>90	3.5	6 (160 cycles)	Zr/Ti in Na°
T-91	"	"	"	1000	.6	>90	3.6	1	Al granules in Na°
T-92	"	"	"	"	"	>90	3.6	4	Al/Hg in Na°
T-88	"	"	"	"	"	>90	3.6	8	$LaCl_3$ in Na°
T-93	"	60 x 30	15	120	1		2.0	44	Failure probably $S^=$ bridge. Resis. incr. ~5% in 44 days.
T-97	"	70 x 30	20	70	1			18	
T-98	"	70 x 50	10	180,850	1,.6		3.0	6	Wet glass + Al in Na° Resist. incr. 50% after 4 days.
T-99	413	70 x 50	10	220	1		1.3	20	Wet glass + Al in Na°, no resis. incr.
T-100	"	"	"	300	1		1.8	22	Wet glass + Al in Na°, no resis. incr.

TABLE I, (Cont'd.)

Cell	Fibers Glass	Fibers Size, μ	Fibers Wall μ	Current Density ma	Cycles, Hrs.	Depth, %	Na°, Column Volms	Life Days	Remarks
T-101	413	70 x 50	10	310	1		1.9	15	NaH/Al in Na°, no resis. incr.
T-102	410	60 x 30	15	70	1		1.1	14	Mg in Na°:Erratic short at fibers.
T-105	406	60 x 30	15	125	4	50	8.0	46	Possibly slight resis. incr.
T-107	"	"	"	"	1	25	4.0	>49	No resis. incr.
T-108	"	"	"	"	4	50	8.0	36	~7% resis. incr.
T-109	"	"	"	"	2	25	4.0	19	No resis. incr.
T-110	"	70 x 50	10	125	2	32	1.1	14	-125 micron spacer.
T-111	"	"	"	"	4	64	2.2	14	-125 micron spacer.
T-113	"	"	"	110	6	85	2.9	7	-125 micron spacer, failed under tube sheet
T-114	413	70 x 30	20	125	1	~ 7	2.0	14	Fiber end failure.
T-115	"	"	"	"	2	~15	4.0	16	Fiber end failure.
T-116	406	70 x 50	10	125	4	45	2.2	9	Probably failed under tube sheet
T-117	"	"	"	"	2	22	1.1	5	Probably failed under tube sheet

TABLE II

FIVE AMPERE-HOUR CELLS

Cell	Fibers Glass	Size, μ	Wall, μ	No.	Leak Rate, Bubbles/ min.	Current amps	Cycle, hrs	Life Days	Remarks
A-134	410	70 x 50	10	3870	2.5	.4	4	5	No resis. incr.; failure is short in foil roll.
A-140	"	60 x 30	15	4800	12	.13	4	23	Resis. incr. 4th day, poor fill; fiber failure.
A-141	"	"	"	"	22	.25	4	10	No resis. incr.; fiber failure under tube sheet.
A-142	406	"	"	5400	20	1.0	4	1.5	No resis. incr.; fiber failure under tube sheet.
A-144	410	"	"	4800	2.5	< .2	4	> 8	Bad internal connector.
A-145	406	"	"	"	10	.2	4	4.5	Fiber failure under tube sheet.
A-146	"	"	"	"	27	-	-	1	Air leak into cell-fiber failure.
A-147	"	70 x 30	20	"	3	< .2	4	25	Poor fill, no BCl_3, resis. incr.
A-148	"	"	"	"	0	.2	4	7	No resis. incr.; lost Na contact.
A-150	413	"	"	5400	40	.3	4	1	Fiber failure.
A-151	"	"	"	"	24	.5	4	> 9	Poor fill, no BCl_3, resis. incr. 4th day.
A-154	"	80 x 50	15	4500	30	.5	4	7	No resis. incr.; failed below tube sheet.
A-161	406	70 x 30	20	4500	4	< .5	4	16	Poor fill, no BCl_3, failed under tube sheet.
A-164	413	80 x 50	15	4500	28	.5	4	8	No resis. incr. failure below tube sheet.

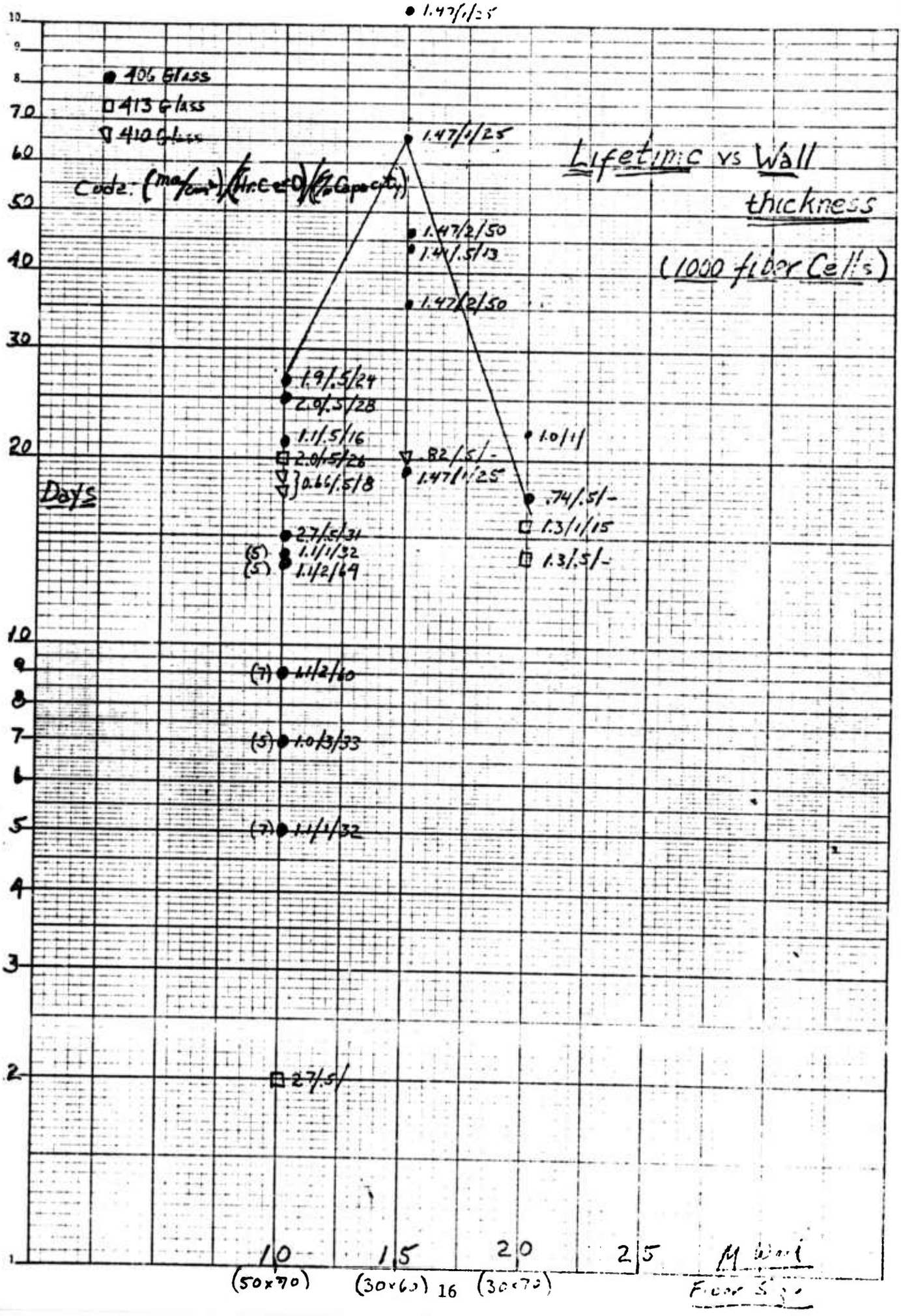
In the last technical report, cell failures were described as generally due to: 1) fiber degradation or failure; 2) tube sheet failure; 3) anode cup failure; or 4) failure due to strains at the tube sheet fiber interface. We no longer have failures due to (2) tube sheet failure or (3) anode cup failure. The 'tube sheet failure' mode was solved by a better understanding of how to fuse the tube sheet into a solid glass mass. With the larger tube sheets, the cumene vehicle must be thoroughly removed before attempting to fuse the solder glass. To do this, the assembly is held under vacuum for at least five minutes at 100-180°C.

The "anode cup failure" mode disappeared when we began to get better sealed cells. This failure was due to air leaking into the operating cells, forming Na_2O which in turn attacked the aluminum anode cup.

Failures are now seen at two sources - - - in the body of the fiber itself, amongst the glass fiber-foil roll, and in the area of the fiber immediately beneath the tube sheet.

The two approaches being used to get longer life cells are: 1) to make thicker walled fibers; and 2) to discover, from systematics of cell operation, what causes the fibers to break.

Effect of Wall Thickness. Graph I shows some data on the effect of fiber wall thickness on the 1000 fiber, 0.4 ampere-hour cells. All cells are included, no matter what the mode of failure. The maximum lifetime of the cells with 10 micron walls is 26-1/2 days while the maximum life of the 15 micron wall cell is over 60 days of continuous charge-discharge and still operating. Both of these cells have about the same depth of discharge and about the same voltage drop across the fiber wall. Generally, the 10 micron wall cells are grouped around 15-25 days and the 15 micron wall fibers are from 35 to over 60 days. The thicker 20 micron wall fibers should be longer lived, but unexpectedly are in the 15-18 day life region. All of the cells made with 20 micron wall fibers, however, failed due to fiber breakage at the very ends of the fibers. This was probably due to


406 Glass
413 Glass
410 Glass
Code: (ma/cm²)/(Hr. C=0)/(% Capacity)
Lifetime vs Wall thickness
(1000 fiber Cells)
Days
1.47/1/25
1.47/2/50
1.4/1.5/13
1.47/2/50
1.9/.5/24
2.0/.5/28
1.1/.5/16
2.0/.5/26
.66/.5/8
.82/.5/-
1.47/1/25
1.0/1/
.74/.5/-
1.3/1/15
1.3/.5/-
2.7/.5/31
(5) 1.1/1/32
(5) 1.1/2/69
(7) 1.1/2/60
(5) 1.0/3/33
(7) 1.1/1/32
2.7/.5/
10
15
20
25
(50×70)
(30×60)
16
(30×70)
Floor Size

the poor seals made when these heavy walled fibers were cut and sealed by the hot gas stream. The formation of weak hooks and ends was described earlier. With adequately sealed fibers, cells made of 20 micron fibers should last over six months of continuous operation.

"Standard" current density across the 10 micron wall fiber is about 2 milliamperes per cm^2. For the same voltage drop across the 15 micron wall, the current density is about 10/15 of 2 or 1.3 ma per cm^2. Therefore, when designing for the same power output at the same voltage efficiency, more glass fibers and glass fiber surface is needed.

Effect of Depth of Discharge. From Graph I, there seems to be no correlation between lifetime and depth of discharge up to at least 50% depth. The "% depth" is based on 100% being the depth for a catholyte of Na_2S_3 to "Na_2S_{20}". The results are not quite so clear as we go to over 90% depth of discharge and charge. Four cells (T-87, 88, 91, & 92) were run to over 90% depth. The maximum life was eight days and the average was five days compared to the twenty day average for the other 10 micron wall cells. These cells, however, were very high rate cells (3 x design) as well as deep cycling. Other cells are now being run to differentiate the effects of high rate and deep cycling.

Effect of "Getter" in the Sodium Anolyte. If deep cycling the cell is causing decreased lifetimes, it could be due to attack on the glass fiber from oxide in the sodium. The oxide would be concentrated in the fibers during discharge of the cell. As sodium is discharged through the walls of the fibers, the oxide which cannot go through the glass is concentrated such that its concentration, C, is

$$C = C_o e^n$$

where C_o is the original concentration and n is the number of "column volumes of sodium discharged".

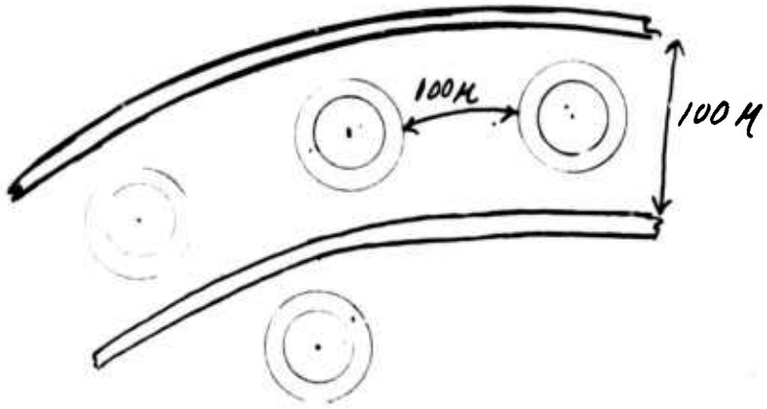
In order to decrease the concentration of oxide, a number of possible "getters" were added to the molten sodium. Among those tried were Zr-Ti alloy, Al granules, Al granules treated with Hg, NaH plus Al, Mg, and $LaCl_3$. These were tried as additives to the sodium in the small T-cells. Some of the cells were run at the very high rates (~20 minutes) and deep cycling and some under normal conditions.

The results for the high rate-deep cycling cells are seen in cells T83, 87, 88, 91 and 92. Life of the cells using Al or Al/Hg is unchanged from the untreated cells (1 to 4 days). Life of the cells using the Zr/TI or $LaCl_3$ was 6 to 8 days, which may or may not be meaningful. Lifetime of cells run under normal conditions was uncharged. We have now stopped using "getters" in the sodium.

Effect of "Column Volumes" of Sodium Discharged. In the first part of this report period there seemed to be a correlation between lifetime and the number of "column volumes" of sodium passed on a discharge cycle. The deeply discharged cells that passed 3.5 to 3.6 column volumes of sodium lasted a shorter time then the cells which passed only 0.4 to 1.4 column volumes in going up to 50% depth of discharge. A possible reason is, as stated above, the concentration of harmful impurities in the sodium anolyte. If this effect were real, it would mean that an important design consideration would be making the internal diameter of the fiber large enough so only a few column volumes of sodium would be discharged per cycle. However, as cells T-105, 107, 108 & 109 indicate, even 4 to 8 column volumes of sodium per cycle do not shorten lifetime of the cell when normal current densities are used. Cell T105 had a lifetime of 46 days of continuous operation at 50% depth of discharge per cycle and passing 8 column volumes of sodium per cycle.

Apparently, there is little or no degradation of the fiber from the sodium side of the cell due to a concentration of impurities.

Effect of Foil-Foil Spacing. The one hour cell design calls for fibers to be about 100 micron apart and the cathode foils to be about 100 microns apart.



The volume element around each fiber contains the amount of sulfur for one hour at the designed current. For a cell designed for longer times, at the same current density on the fiber, the volume element must be larger. Experiments have been begun on increasing the foil to foil distance from 100 micron to larger spacings.

Preliminary results indicate no change in cell lifetime. An effect is noted, however, when the cell is first started after being loaded with sulfur. With 100 micron spacing the cell resistance drops to an operable range in an hour or less and is almost at its final internal resistance in a few hours. With 125 micron spacing, several hours of discharge are required to bring the cell to an operable range and the final internal resistance is not reached until a much longer time (1 day). We are now determining the degree of charge such a cell can be brought to before the cell internal resistance doubles due to the resistance of the sulfur. With the 100 micron spacing, the cell can be charged to a composition of approximately "Na_2S_{20}" before this happens. With wider spacings it may be less.

Effect of Fiber Glass Composition. The 406 glass used for the fiber at the beginning of this period contains excess NaCl to enhance conductivity. We had concern that the chloride ion might migrate out of the structure weakening the glass. Glass was made without the chloride (410) and fibers and cells made from this. No increase in lifetime was seen. Glass resistivity was increased about fifteen times by leaving out the NaCl, so it was an undesirable step and was discontinued when no lifetime enhancement was obtained.

The ratio of Na_2O to B_2O_3 in the 406 glass puts it on the edge of glass stability. It is very close to a crystallization range. Another glass was made which contained slightly more B_2O_3, hence was more stable. Fibers and cells were made from this glass (413). These cells did not show longer life than cells made with 406 glass. The excess B_2O_3 resulted in a higher resistivity glass (2X), so this glass was discontinued.

Change of Cell Resistance with Time. The increase of cell internal resistance with time is somewhat varied. One T-cell has operated over 49 days continuously on two hour cycles (T107) with no increase in internal resistance. Another cell (T105) has operated on four hour cycles for 46 days with no definite resistance increase. Other cells have shown an increase. Cell T-93, the same construction as the T105 & 107 cells, had a 5% resistance increase in 44 days.

At very high rates and/or deep charge-discharge, the cell resistance seems to go up faster. Cell T-98, operating at about three times normal current density and relatively deep cycling had an increase in resistance of about 50% after 4 - 5 days operation. We do not know yet whether this is a consequence of high rate (high current density or voltage drop) or deep cycling or neither.

We do get a relatively rapid increase in cell resistance within 5 - 7 days if the cell assembly is not treated with BCl_3 gas before being loaded with Na and sulfur. This is possibly due to residual water or organics (removable by BCl_3) which slowly react to separate sodium columns, etc.

Effect of Current Density. Graph I indicates that there is no correlation between lifetime and current density across the fiber in the range of 0.6 to 2.0 ma per cm^2 across the fiber. The normal current density for the 10 micron wall fiber is about 1.5 ma per cm^2. The high rate, deep cycled cells mentioned before and shown in Table I had much shorter lifetimes at their current densities of up to 8 ma per cm^2, but whether the shorter lifetime is due to the high current density or deep cycling is not yet known.

Cell Operating Characteristics Now Being Investigated. Cells are now being operated to separate the effects of deep cycling and high rate. Better 20 micron wall fibers have been drawn and made into cells and these cells are running to determine their lifetimes. Data is being collected on the effect of foil-foil spacing in the 5 ampere-hour cells on cell resistance in the fully charged state.

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3/12/74